Formal Valence, d Occupation, and Charge-Order Transitions

Y. Quan
Department of Physics, University of California Davis

V. Pardo
Departamento de Física Aplicada, Universidade Santiago de Compostela, Spain, and Department of Physics, University of California Davis

W. E. Pickett
Physics Department, University of California Davis

(Dated: April 9, 2012)

While the formal valence concept has been tremendously important in materials physics, its very loose connection to actual charge leads to difficulties in modeling its consequences and interpreting data correctly. We point out, taking several transition metal oxides (La_2VCuO_6, $YNiO_3$, $CaFeO_3$, $AgNiO_2$, V_4O_7) as examples, that while dividing the crystal charge into atomic contributions is an ill-posed activity, the $3d$ occupation of a cation (and more particularly, differences) is readily available in first principles calculations. We discuss these examples, which include distinct charge states and charge-order (or disproportionation) systems, where different "charge states" of cations have *identical* $3d$ orbital occupation. Implications for theoretical modeling of such charge states and charge-ordering transitions are discussed.

Spin ordering, and often orbital ordering, is normally unambiguous, as these properties are subject to direct observation by magnetic and spectroscopic measurements, respectively. Charge ordering and the formal charge of an ion is rarely measured directly, and the formal charge of an ion in the solid state can be a point of confusion and contention. Valence, oxidation number, and formal charge are concepts borrowed from chemistry, where it is emphasized they do not represent actual charge[1, 2] and have even been labeled hypothetical.[1] As the interplay between spin, charge, orbital, and lattice has become more closely watched[3] and acknowledged to be a complex phenomenon, the issue of disproportionation and CO has become entrenched as the explanation of several high profile metal-insulator transitions.

Charge density is a physical observable of condensed matter, and the desire to assign charge to atoms has evident pedagogical value, so several theoretical approaches have been devised to share it amongst constituent nuclei. Mulliken charge population, which socializes shared charge (divides it evenly between overlapping orbitals) is notoriously sensitive to the local orbital basis set that is required to specify it. Bader charge analysis[4] applies a topological property of the full charge density (the surface of vanishing density flux) to separate the charge, and is explicitly sensitive to interatomic separations and resulting changes in hybridization and the atomic regions have unusual shapes. Born effective charges are dynamical properties and are often quite different from any conceivable formal charge or actual charge. Dividing the static crystal charge density into atomic contributions is, in fact, an ill-defined activity.

However, a possibility that has not been utilized is that, in many and perhaps most of ionic crystals where one would like to base an understanding and a faithful model on charges and their differences, there is a relevant quantity that is well defined: the d occupation n_d (and perhaps for anions, the p atomic orbital occupation). This quantity is moreover what the physical picture of formal charge or oxidation state brings to mind. We take $3d$ cations in oxides to illustrate our point. These cations, in their various charge states, have maxima in their spherically averaged radial density $\bar{\rho}(r)$ in the range 0.6-0.9 a_o. At this short distance from the nucleus, the only other contribution to the density is the core contribution, which can be subtracted out and is unchanged during chemical processes or charge ordering. Most relevant to the understanding of charge-order driven transitions and disproportionation is the (actual or relative) *difference* in occupations Δn_d, which is given directly by the difference in the radial $3d$ densities at their peaks, where there are no competing orbital occupations to confuse charge counting. The fact that there is this specifically defined $3d$ occupation provides a basis for forming a faithful picture of charge ordering and of characterizing formal valence differences more realistically. We consider our calculational results[5, 6] for a selection of systems, then discuss some of the implications.

$\underline{La_2VCuO_6}$ (LVCO) is a double perovskite compound comprising a vivid and illustrative example. Our earlier study[7] revealed two competing configurations for the ground state, with bands shown in Fig. 1. Using conventional identifications, one is the V^{4+} d^1, Cu^{2+} d^9 magnetic configuration, identified as such because (1) there is one band of strong V d character occupied and one band of strong Cu d character unoccupied, and (2) the moments on both V and Cu, 0.7 μ_B, are representative of many cases of spin-half moments reduced by hybridization with O $2p$ orbitals. The other configuration is nonmagnetic $d^0 - d^{10}$: all Cu d bands are occupied, all V d bands are unoccupied – a conventional ionic band insulator in all respects. The identification of formal valence (or oxidation state) is crystal clear.

The radial charge densities of V and of Cu for both configurations reveal an unsettling feature: the actual $3d$ occupations n_d of each of V and Cu are *identical for both configurations*, in spite of the unit difference in their formal charges. (Identical in this paper means to better than 0.5%.) Thus ions with identical $3d$ charge can behave as if they comprise distinct charge states. Changes in spin-orbital occupations, which quantify spin, orbital, and charge differences between the two states, can be quantified by the LDA+U spin-orbital occupations. For the V d^1 d_{xy} (Jahn-Teller split) orbital, the majority-minority difference is 0.70, which accounts for all of the moment. The difference of 0.65 between d_{xy} and each of the other t_{2g} characterizes the Jahn-Teller distortion. The increase in charge of the d_{xy} orbitals (both spins), 0.55, compared to the d^0 state, is taken more or less uniformly from all other (nominally unoccupied) spin orbitals. Similarly for Cu, the d^9 hole results from a difference of charge in the minority $d_{x^2-y^2}$ orbital of 0.6, with the other charge being distributed nearly uniformly over the other nine (nominally fully occupied) spin-orbitals. In both cases the moment arises entirely from the single magnetic orbital, all other orbitals are unpolarized. This happens, conspicuously, with *no change* in n_d for either V or Cu. Charge is redistributed to one orbital from the others, and strongly spin-imbalanced within that orbital. We look at additional cases before addressing some of the implications.

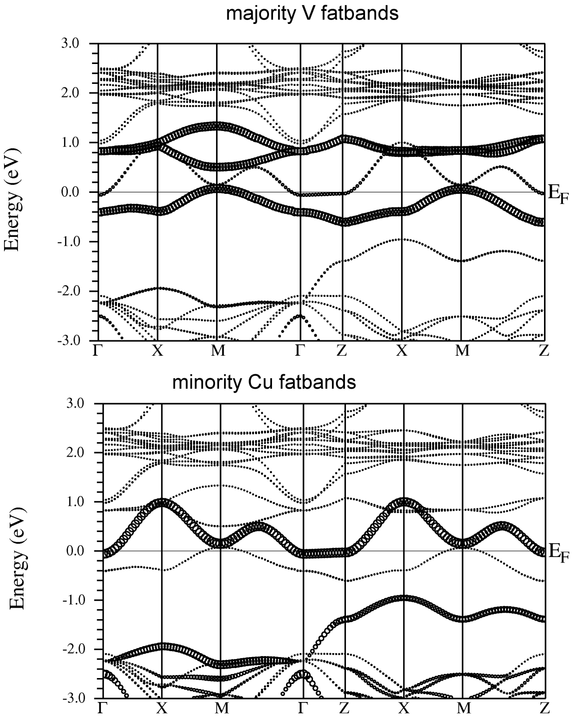

FIG. 1: (Color online) Top: bands near the Fermi energy/bandgap in the $d^1 - d^9$ magnetic, nearly Mott insulating, configuration of La_2VCuO_6. The d_{xy}-up band is correlation-split off from the other two t_{2g} bands and fully occupied. Bottom: the Cu fatbands for the same system, showing one unoccupied Cu minority $d_{x^2-y^2}$ band correlation-split from the d_{z^2} band. The other d bands fall outside this energy range.

Rare earth ($\mathcal{R}$) nickelates $\mathcal{R}NiO_3$ display a first order structural and metal-insulator transition (MIT) of great current interest, The $Pbnm$ ($GdFeO_3$ structure) $\rightarrow P2_1/n$ transformation results in a large $Ni1O_6$ and a small $Ni2O_6$ octahedron, with Ni-O distances of 2.015±0.015 Å and 1.915±0.025 Å, respectively, that are not otherwise strongly distorted; see the inset of Fig. 2. At a temperature that varies smoothly from 600K to 300K with increasing $\mathcal{R}$ ionic radius, the resistivity of these nickelates drops sharply.[8, 9] We focus on $YNiO_3$; with its small ionic radius, it is one of the more strongly distorted, and the resulting narrowed bandwidths make it more prone to strong correlation and charge order tendencies.[10] Structural changes at the MIT have been studied extensively,[8, 11–14] which together with x-ray absorption spectral splittings[15–17] have been interpreted in terms of charge disproportionation (or CO) $2Ni^{3+} \rightarrow Ni^{3+\delta} + Ni^{3-\delta}$, with $\delta \approx 0.3$ for $YNiO_3$.[15]

This MIT in the nickelates has been recognized as paradigmatic by theorists. Mizokawa, Khomskii, and Sawatzky modeled this system[18] with a multiband Hartree-Fock model in the charge-transfer regime and found evidence for CO on the *oxygen* sublattice for larger $\mathcal{R}$ cations, but concluded that $YNiO_3$ was representative of a CO transition on the Ni sites. Mazin *et al.*[10] surveyed the competition between Jahn-Teller distortion of the d^7 ion and charge ordering and also concluded that $YNiO_3$ is a prime example of a CO $d^6 + d^8$ system. Lee *et al.* have investigated[19] a two band model for this system with a CO interaction in mean field, emphasizing CO effects. On the other hand, Yamamoto and Fujiwara[20] (YF) reported a very small (∼0.03 e^-) density functional based charge difference.

For the assumed (for simplicity) ferromagnetic order the calculated Ni1 and Ni2 moments are 1.4 and 0.65 μ_B respectively for $YNiO_3$ and several other members of this class, so these values are not very sensitive to the magnitude of the distortion.

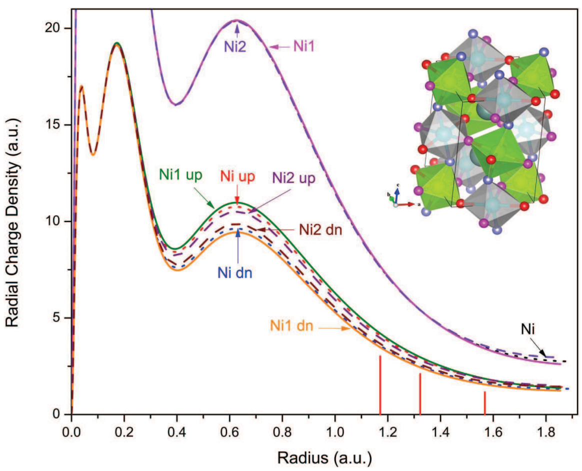

FIG. 2: (Color online) Radial charge density (upper curve) of $YNiO_3$ for $Pbnm$ Ni and $P2_1/n$ Ni1 and Ni2, showing there is no different at the peak, which reflects the $3d$ occupation of the ion; a small difference shows up near the sphere boundary. The spin decompositions give easily visible differences. The vertical lines at the bottom right indicate conventional Ni^{4+}, Ni^{3+}, and Ni^{2+} ionic radii (see text). Inset: Structure of the broken symmetry $P2_1/n$ phase, showing the rotation in the $a-b$ plane and tilting along the c axis of the NiO_6 octahedra (Ni is inside) and the (π, π, π) ordering of the Ni1 and Ni2 octahedra.

They coincide with the values obtained from neutron diffraction,[11] 1.4(1) and 0.7(1) μ_B respectively, in the magnetically ordered phase. It is intriguing that the same moments were obtained in fully relaxed $LaNiO_3/LaAlO_3$ monolayer superlattices.[21] The electronic state for $YNiO_3$ with this FM ordering is a narrow gap insulator, consistent with the common characterization of these nickelates as charge-transfer insulators, rather than Mott insulators, in which the gap is determined by the (small) charge transfer energy rather than the (large) interaction U.

The $3d$ occupations, obtained as above directly from the maximum in the radial charge density plots in Fig. 2, are identical for Ni1, Ni2, and the single Ni site in the high temperature phase: there is no $3d$ charge change, or disproportionation, at the transition. The majority and minority radial densities and integrated charges of course differ (see Fig. 2) as they must to give the moment, but the total $3d$ occupation is inflexible. This constancy of the $3d$ occupation across the transition, and equality for Ni1 and Ni2, is inconsistent with microscopic disproportionation.

To illustrate the spin-orbital spectral density redistribution, the projected densities of states are shown in Fig. 3. First, we note that while the t_{2g} states are always filled, there is considerable shift of spectral weight across 4 eV, a reflection of the different sizes of the octahedra, which affect the amount of hybridization and on-site energy. The Ni1 site acquires a considerable spin asymmetry due to Hund's coupling within e_g states. The spectral distribution is non-intuitive: e_g weight from -5 eV spin-down is transferred to -1 eV spin-up. The majority e_g states just below the gap are strongly Ni1 in character, while the unoccupied bands just above the gap are primarily Ni2. Such behavior is expected for different charge states, similarly to behavior in La_2VCuO_6 above; however, the charge is identical. The main differences between Ni1 and Ni2 show up in the *unoccupied* e_g states: the Ni1 spin splitting is 3.5 eV, a reflection of the on-site repulsion that opens the Mott gap in the majority e_g states, and the Hund's coupling contribution. The origin of the Ni2 moment is murky, not identifiable with any occupied spectral density peak. In a $Ni^{2+} + Ni^{4+}$ charge ordered picture, Ni2 would be nonmagnetic. Not only is this behavior not consistent with a CO picture, it involves redistribution not accounted for in any simple model. In spite of identical $3d$ charges, the Ni1 and Ni2 core energies differ by up to 1.5 eV.

$\underline{CaFeO_3}$, another perovskite that displays the same $Pbnm \rightarrow P2_1/n$ structural change at T_{MI} as the nickelates, is also explained[22] in CO language that invokes the high (penta)valent state Fe^{5+}. Analogously to $YNiO_3$, we obtain identical $3d$ occupations for Fe1 and Fe2 ions. Quantum chemical embedded cluster calculations[23] and LDA+U studies[24–26] had noted that the Fe charge in both "disproportionated" sites differed little, but neither quantified the occupation to the degree we have done for $YNiO_3$ and $CaFeO_3$. The pentavalent state of Fe has most often been identified from Mössbauer isomer shift data, but Sadoc *et al.*[23] concluded the difference in isomer shift is primarily a measure of the covalency (Fe-O distance) rather than any real charge on Fe.

$\underline{AgNiO_2}$, a triangular, magnetically frustrated lattice compound with nominal Ni^{3+} ions, undergoes a structural transition at 365 K although remaining metallic.[27–30] Three inequivalent Ni sites arise, with a high spin Ni1 ion in an enlarged octahedron and two low spin Ni2, Ni3 = Ni2,3 ions in small octahedra. Based on the structural changes (which could be quantified by bond valence sums), the magnetic moments, and resonant x-ray scattering that confirms a calculated ~1 eV in core level energies between Ni1 and Ni2,3, this transition has been welcomed as the first realization of such a $3e_g^1 \rightarrow e_g^2 + e_g^{0.5} + e_g^{0.5}$. Furthermore, using the charge difference per unit core level splitting of 0.66 e/eV led to an inferred charge disproportionation of $\sim 1.65e$, *i.e.* $Ni1^{2+} + Ni2{,}3^{3.5+}$.

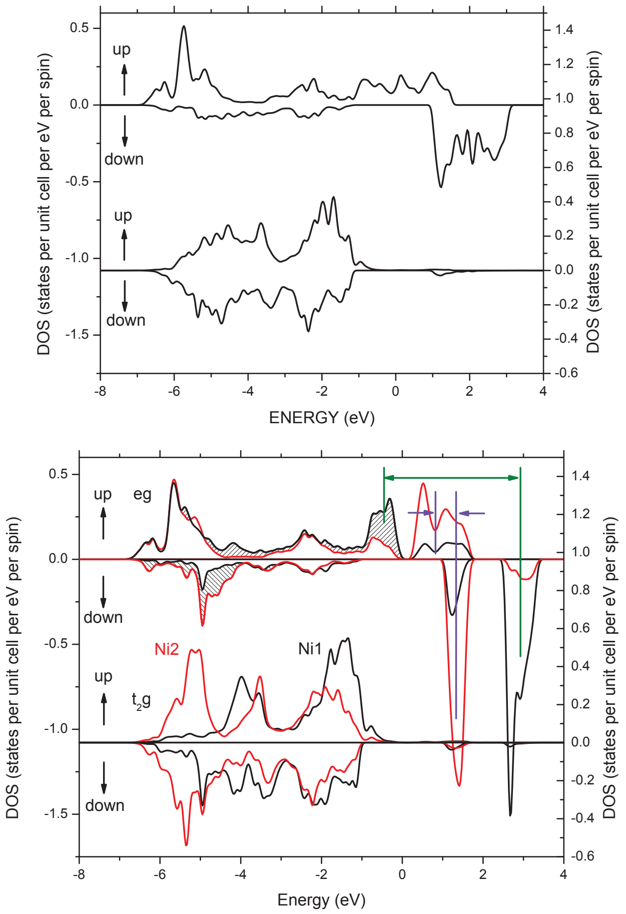

FIG. 3: (Color online) Top panel: spin-decomposed Ni t_{2g} and e_g density of states for the metallic *Pbnm* phase of YNiO$_3$, which is half-metallic due to the artificial FM order. Middle panel: analogous plot for the Ni1 and Ni2 ions in the insulating $P2_1/n$ broken symmetry phase. The hashed regions illustrate the spectral origin of the enhanced moment of Ni1 relative to Ni2. The horizontal arrows illustrate the large difference in spin splittings, the result of the combination of Hund's coupling and Coulomb U=5.7 eV.

We have reproduced several of the first principles results presented in corroboration of the CO interpretation.[27, 30] Note that, due to the metallic character of AgNiO$_2$, no Coulomb repulsion U has been used or needed. The calculations reproduce a large moment ($> 1\mu_B$) on high-spin Ni1 and very weak moments ($\sim$0.1 μ_B) on low-spin Ni2,3 ions. We have obtained the 3d occupations from the radial densities as above; remarkably, although as found for the systems mentioned above, n_d for the three sites are *identical*, there is no Ni charge difference. Our calculated core level differences, 0.6-0.8 eV, are roughly consistent with those reported earlier,[30] ($\sim$1 eV), but interestingly are more nearly half the differences for YNiO$_3$ (above) where the amount of charge disproportionation was inferred to be much smaller.

V$_4$O$_7$ represents another oxide explained by CO-driven MIT. It is structurally more involved, but first principles calculations of moments and geometries again have produced several results corroborating the experimental data[31, 32] and used to support CO into "V^{3+}" and "V^{4+}" sites. As in the instances above, we find no differences in n_d: the occupations are indistinguishable. The site energy differences, measured by differences in 1s, 2s, 2p core levels, differ by 0.9-1.0 eV for two sites, similar to the nickelates. The interplay of orbital order, structural distortions, and possible spin-singlet formation of half of the V ions provide a rich array of degrees of freedom, which can operate without need for disproportionation.

Implications. We have shown that, for several instances of CO transitions and the two charge states of La$_2$VCuO$_6$, there is no different in the 3d occupation (thus, the charge) for the different charge states. Luo *et al.* concluded[33] for doped manganites that the variation of the 3d charge on Mn with different charge states was negligible, and that oxidation states were more directly related to orbital occupancy in that system. The origin of the differing characteristics of the ions, and the meaning of charge state and disproportionation, requires clarification.

The inflexibility of the 3d occupation, now documented in several 3d oxides, indicates that charge fluctuations in these systems are too high in energy to be complicit in these phase transitions, so alternative driving forces must be sought. Displacements $\sim$0.1Å as shown by O ions are normally unfavorable energetically (high symmetry oxides are common). However, ion size mismatch can make the symmetric phase unstable, *viz.* the tolerance ratio in perovskites that is a good predictor of structural distortions. The ionic radii that are marked in Fig. 2 regularize a great deal of structural data based on identified "charge states," commonly identified as such because of the structural differences, that is, the oxygen environment. The difference for Ni^{4+} vs. Ni^{2+}, about 0.15Å, characterizes the Ni-O separation rather than any difference in ionic charge.

In both the nickelates and V$_4$O$_7$ there is evidence of distinct metal sites *above* the transition, in the (on average) symmetric phase. For example, x-ray absorption spectra[16, 17] reveal that signatures of Ni1 and Ni2 sites persists continuously across the MIT, and both sites also remain when driven across the phase boundary by pressure.[34] As we have shown, the coordination accounts for on-site energy differences of $\sim$1 eV in spectra that have often been used to support disproportionation. The MITs in some of these materials may be primarily order-disorder type; the onset of long-range order in nickelates results in carrier localization and gap formation, ergo a MIT.

These materials are magnetic, so Hund's rule energies which are quadratic in the moment favor a large and small moment over two equal moments, a feature frequently used to support disproportionation. Different O octahedron sizes encourage different moments by modulating metal-oxygen hybridization and orbital occupations. The site energy difference will couple to the change in M-O hybridization, especially so in the charge-transfer regime (nickelates and cuprates).

In keeping with the language, we suggest that CO should be accepted as a driving force, hence an interpretation, of a transition only if a discernible charge difference exists; otherwise, the underlying mechanisms should be identified. We do not suggest that CO transitions do not exist in $3d$ oxides; indeed the best way to clarify the physics of these systems will be to identify examples of charge disproportionation and make comparisons. Formal developments should be pursued as well; for example, Jiang *et al.* have provided a specification[35] of integer charges in an insulator that they propose as oxidation states. Based on integration over a configuration space path of the dynamic Born effective charge, their expression assigns (in principle) an integer charge to each atom in any insulator. More experience will be needed to learn how to interpret their definition.

A logical extension beyond comparing differences in $3d$ occupations is to identify the absolute $3d$ occupations, which we are initiating. We find, for example, that the Ni^{3+} ions have identical occupations in $YNiO_3$ and $AgNiO_2$, which is not at all necessary, and the value is $n_d \approx 8$ rather than the idealized value of 7 for a d^7 ion. In La_2VCuO_6, $n_d^V \sim 1.9, n_d^{Cu} \sim 8.9$ for both configurations; note that the V occupation is not near either "valence state." Understanding of such occupations will surely advance identification of, and understanding of, microscopic mechanisms of MITs.

Acknowledgment. Work at UC Davis was supported by DOE grant DE-FG02-04ER46111. V.P. acknowledges support from the Spanish Government through the Ramón y Cajal Program.

[1] G. Parkin, J. Chem. Educ. **83**, 791 (2006).

[2] D. W. Smith, J. Chem. Educ. **82**, 1202 (2005).

[3] D. I. Khomskii and G. A. Sawatzky, Solid State Commun. **102**, 87 (1997).

[4] R. F. W. Bader, *Atoms in Molecules: a Quantum Theory* (Oxford University Press, New York, 1990).

[5] The density functional based linearized augmented plane wave code WIEN2K[6] has been used in our calculations, where we have applied correlation corrections (LDA+U) as is usually necessary to describe $3d$ oxides. Computational methods are as described in Ref. [7].

[6] K. Schwarz and P. Blaha, Comp. Mat. Sci. **28**, 259 (2003).

[7] V. Pardo and W. E. Pickett, Phys. Rev. B **84**, 115134 (2011).

[8] J.L. García-Muñoz, J. RodríGE-Carvajal and P. Lacorre, Physica B **180**, 306 (1992).

[9] J. B. Torrance *et al.*, Phys. Rev. B **45** 8209 (1992).

[10] I. I. Mazin *et al.*, Phys. Rev. Lett. **98**, 176406 (2007).

[11] J.A. Alonso *et al.*, Phys. Rev. Lett **82**, 3871 (1999).

[12] J. A. Alonso *et al.*, Phys. Rev. B **61**, 1756 (2000).

[13] J. A, Alonso *et al.*, J. Am. Chem. Soc. **121**, 4754 (1999).

[14] I. Vobornik *et al.*, Phys. Rev. B **60**, R8426 (1999).

[15] U. Staub *et al.*, Phys. Rev. Lett. **88**, 126402 (2002).

[16] C. Piamonteze *et al.*, Phys. Rev. B **71**, 012104 (2005).

[17] M. Medarde *et al.*, Phys. Rev. B **80**, 245105 (2009).

[18] T. Mizokawa, D. I. Khomskii, and G. A. Sawatzky, Phys. Rev. B **61**, 11263 (2000).

[19] S.-B. Lee, R. Chen, and L. Balents, Phys. Rev. B **84**, 165119 (2011).

[20] S. Yamamoto and T. Fujiwara, J. Phys. Soc. Japan, **71**, 1226 (2002).

[21] A. Blanca-Romero and R. Pentcheva, Phys. Rev. B **84**, 195450 (2011).

[22] M. Takano *et al.* Phys. Rev. Lett. **67**, 3267 (1991).

[23] A. Sadoc, C. de Graaf, and R. Broer, Phys. Rev. B **75**, 165116 (2007).

[24] J. B. Yang *et al.*, J. Appl. Phys. **97**, 10A312 (2005).

[25] T. Saha-Dasgupta, Z. S. Popović, and S. Satpathy, Phys. Rev. B **72**, 045143 (2005).

[26] J. Matsuno *et al.*, Phys. Rev. B **66**, 193103 (2002).

[27] E. Wawrzyska *et al.*, Phys. Rev. Lett. **99**, 157204 (2007).

[28] E. Wawrzyska *et al.*, Phys. Rev. B **77**, 094439 (2008).

[29] J.-H. Chung *et al.*, Phys. Rev. B **78**, 214417 (2008).

[30] G. L. Pascut *et al.*, Phys. Rev. Lett. **106**, 157206 (2011).

[31] A.S. Botana *et al.*, Phys. Rev. B **84**, 115138 (2011).

[32] J.-L. Hodeau and M. Marezio, J. Solid State Chem. **23**, 253 (1978).

[33] W. Luo *et al.*, Phys. Rev. Lett. **99**, 036402 (2007).

[34] A. Y. Ramos *et al.*, arXiv:1112.4365.

[35] L. Jiang, S. V. Levchenko, and A. M. Rappe, arXiv:1106.2836.